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Zirconium Oxide Nanostructures Prepared by Anodic Oxidation

Ying Yi Dang, M.S. Bhuiyan, and M. Parans Paranthaman

ABSTRACT

Zirconium oxide is an advanced ceramic material highly useful for structural and electrical applications because of its high strength, fracture toughness, chemical and thermal stability, and biocompatibility. If highly-ordered porous zirconium oxide membranes can be successfully formed, this will expand its real-world applications, such as further enhancing solid-oxide fuel cell technology. Recent studies have achieved various morphologies of porous zirconium oxide via anodization, but they have yet to create a porous layer where nanoholes are formed in a highly ordered array. In this study, electrochemical methods were used for zirconium oxide synthesis due to its advantages over other coating techniques, and because the thickness and morphology of the ceramic films can be easily tuned by the electrochemical parameters, such as electrolyte solutions and processing conditions, such as pH, voltage, and duration. The effects of additional steps such as pre-annealing and post-annealing were also examined. Results demonstrate the formation of anodic porous zirconium oxide with diverse morphologies, such as sponge-like layers, porous arrays with nanoholes ranging from 40 to 75 nm, and nanotube layers. X-ray powder diffraction analysis indicates a cubic crystallographic structure in the zirconium oxide. It was noted that increased voltage improved the ability of the membrane to stay adhered to the zirconium substrate, whereas lower voltages caused a propensity for the oxide film to flake off. Further studies are needed to define the parameters windows that create these morphologies and to investigate other important characteristics such as ionic conductivity.

Introduction

The fabrication of large areas of porous, high aspect-ratio nano-sized structures has attracted considerable scientific interest as its potential applications, which range from nanoscale templating to optical, electronic, and micromechanical devices, are being realized. The challenge is to overcome the difficulties of conventional lithographic processes in the production of such structures. One promising approach is to use electrochemical techniques [1]. They are generally straightforward and relatively inexpensive, can be performed near room temperature on a large scale, can deposit uniformly on complex shapes, and the morphology and thickness of the structures can be tuned by the electrochemical parameters and processing conditions such as electrolyte solutions, pH, voltage, temperature and duration.

Zirconium oxide possesses many highly desired materials qualities useful for structural and electrical applications such as fracture toughness, chemical robustness, thermal stability, and biocompatibility. It is already used as catalyst supports [2, 3], chemical sensors [4], thermal barrier coatings, and transformation-toughened materials. If highly-ordered porous zirconium oxide membranes can be successfully formed, this will expand its real-world applications, such as further enhancing solid-oxide fuel cell (SOFC) technology. In the case of the SOFC, it would improve the efficiency as a catalytic material by increasing its surface area with porous nanostructures. To this end, efforts have been placed

on finding ways to create porous zirconia with methods such as template synthesis [5] and electrolytic deposition [6–9].

Anodic oxidation is one particular electrochemical method that has generated significant research effort [10–12] towards investigating the synthesis of ordered oxide structures on metallic surfaces other than zirconium, like Al_2O_3 on aluminum [13, 14]. In this method, two electrodes (one electrode is the metallic surface to be anodized, and the other, usually platinum, serves as the counter and/or reference electrode) are immersed in an electrolyte bath and suspended from wires connected to a DC power supply. Achieving the desired reaction products at the exposed surface is highly dependent on the details of manipulating the chemistry of the metal-electrolyte interface with various combinations of electrochemical parameters. Recent studies have achieved various morphologies of porous zirconium oxide using anodic oxidation [15–18], but they have yet to create a porous layer where nanoholes are formed in an extremely highly ordered array, e.g. a honeycomb structure. Additionally, many questions remain open about the evolution of the nanostructures' morphology and the establishment of the self-organization process [19]. The purpose of this research was to study the formation of porous zirconium oxide structures via anodization, gain an understanding of the formation mechanisms, explore the properties of anodized zirconium, and to continue to test the effects of different permutations of the processing conditions. Plots of anodization current versus, XRD scans and SEM images are used for this discussion.

Materials and Methods

Zirconium (99.98% purity, Aldrich, USA) substrates of 0.75 cm x 2.5 cm were cut from a zirconium sheet of 100 or 25 micron thickness. They were prepared for the electrochemical anodization by first sonicating in acetone for degreasing purposes, then rinsing with deionized water, and finally dried with nitrogen gas. A pure platinum foil served as the counter electrode in the electrochemical cell. Electrolyte bath of 1M $(NH_4)_2SO_4$ + 0.5% NH_4F was prepared at room temperature from analytical grade chemicals and deionized water.

The electrochemical treatment was carried out at room temperature and consisted of the two electrodes immersed in the electrolyte and externally connected to a DC power supply (Agilent E3612A or VersaSTAT 3). Figure 1 shows the basic experimental set-up used for this study. The anodizing area of the zirconium foils is approximately 1.4 cm^2. Current-time measurements were recorded during the treatment. After the electrochemical deposition, the sample surface was immediately rinsed with de-ionized water and then streamed with nitrogen gas to prepare for characterization.

X-ray diffraction (XRD) was used to identify the crystal structure of the resulting ZrO_2 films. XRD was performed with a scanning rate of 0.05 degrees per minute using CuKα radiation with a wavelength of approximately 1.5 Å. The 2θ measurement range varied from 25° to 85°. The actual structure and surface morphology were characterized using scanning electron microscopy (SEM). The cross-section of the samples was also examined. For investigating the effect of annealing, samples were either pre-anodization annealed with Ar at 900°C for 1 hour, or post-anodization annealed with O_2 also at 900°C for 1 hour, and then compared to samples that were processed under identical conditions without annealing.

Figure 1. The anodization setup features a DC power supply, an electrolyte bath, and two electrical wires suspending two electrodes in the electrolyte bath. The black lead holds the Pt counter electrode, and the red one holds the zirconium foil to be anodized.

Results and Discussion

Analysis of Transient Current

By observing the transient current for different runs, a better understanding of the mechanics of anodization can be obtained. Figure 2 shows the current-time behavior for three different anodization runs. All show that after extended constant potential anodization times, all systems experience a decline in current due to the increase in both the oxide layer as an electrical barrier and the diffusion length for the ionic species in the electrolyte bath [20]. Comparing plots for two different voltages, 30 volts (Figure 2a — plot a) and 50 volts (Figure 2a — plot b), it shows that the higher the applied voltage, the longer it takes for the current to die off and the higher the current at all times because the rates of oxidation are higher and the drift of ions are faster under higher applied potentials. It is evident from the particularly rapid fall-off

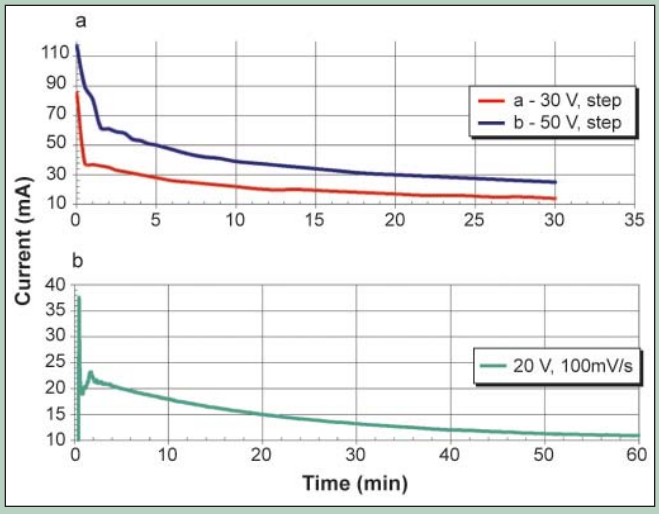

Figure 2. The transient current for (a) 30 V, step and 50 V, step, and (b) 20 V, 100 mV/s.

in current during the first few minutes that the formation of a non-porous compact layer of oxide is the dominant process and hence acts as a barrier layer before any nanostructures have begun to form and compete with the barrier. After those few minutes, the current behavior declines more steadily, thus signifying that it has entered the stage where the compact oxide layer gives way to the porous structures that are taking shape.

In order to better discern the stages of anodization, the electric potential was applied by sweeping from an open circuit potential to a final value of 20 volts at a rate of 100 mV/s and then followed by holding the potential at 20 volts. As seen in Figure 2b, the current during this type of application deviates twice from exponential decay. It initially increases as the applied potential is ramped and then quickly drops and increases again, which marks the transition to a perforated and porous oxide layer. The second increase can be explained by the oxide layer being weakly dissolvable in the presence of the fluoride additives, which creates locally varying film thicknesses. A self-catalyzing effect occurs where the pits or perforations that are created concentrate the electric fields that spur local acid corrosion and also enhance ion drifts [21]. Only after this random growth stage and the pores begin to compete with each other do we observe the usual steady decrease in current, so this second spike in current readings followed by the return to steady decline indicates that the system has entered the pore formation regime [14, 21, 22], which continues until the system is turned off or the pores have reached a final geometry.

XRD Analysis

With XRD analysis, the various signature peaks like ZrO_2 (111) and ZrO_2 (220) as shown in Figure 3 indicate that all the non-annealed ZrO_2 films developed a cubic crystallographic structure directly after anodization. This is consistent with previous literature that reported that the cubic zirconia structure was predominant in compact oxide layers formed in a variety of electrolytes [23]. This is noteworthy because zirconia's naturally occurring form at room temperature is monoclinic and would usually require the addition of dopants such as yttrium to stabilize the cubic phase. Hence, the fact that the zirconia nanostructures have a cubic crystalline structure directly after anodization (Figure 3a) without the need for stabilizers or annealing is of a particular advantage in applications that are sensitive to thermal treatments because cubic zirconia has low thermal conductivity.

In the same figure, the XRD plot of Ar pre-anodization (Figure 3b) annealing shows more intense peaks. This signifies that pre-annealing with argon gas is successful in re-crystallizing and removing the deformities and internal stresses of the pure zirconium foils because if all other conditions are identical, these higher peaks of the ZrO_2 and its parent substrate can only be explained by fewer crystal defects and a more organized structure. However, post-anodization annealing with O_2 reveals completely different peaks (Figure 3c) and corresponds to ZrO_2 that is monoclinic. This indicates that during the annealing process, grain growth and the associated volume expansion causes the cubic phase to convert to monoclinic. The sample has been observed, however, after O_2 annealing to be extremely brittle or cracked after it has cooled from the high annealing temperature, which indicates that the transformation from cubic to monoclinic induces significant stresses on the crystalline structure.

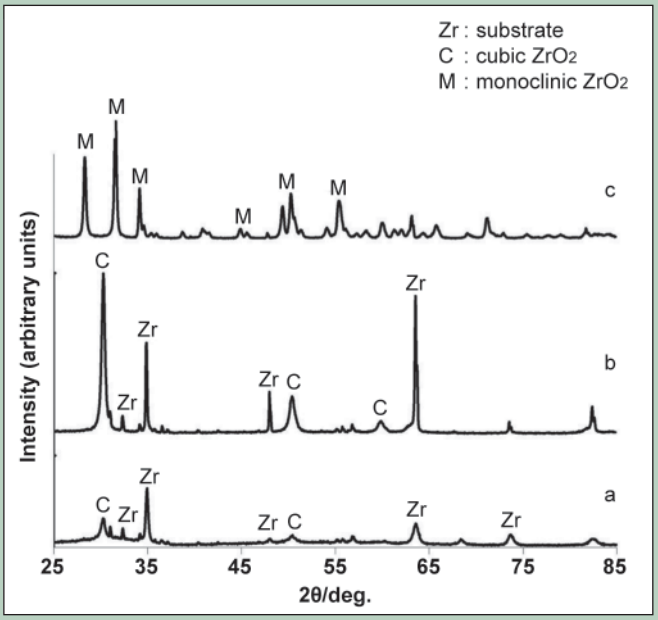

Figure 3. XRD chart for the zirconia (a) without annealing, (b) with pre-anodization annealing with Ar, and (c) post-anodization annealing with O_2.

SEM Analysis

Results of SEM analysis reveal a variety of nanostructures (Figures 4–5), from porous array-like structures, to tubular, to sponge-like, to "mixed". TEM images of the cross section of two particular samples that were anodized for 30 minutes but created at different voltages are shown in Table 1. It indicates the formation of ZrO_2 film on both sides of the substrate. Work is ongoing to define which parameters are specific to the types of structures that have been observed, however, the samples with morphologies possibly viable for application can be seen in Figures 4a and 4b: the semi-ordered nano-hole porous arrays of approximately 40 nm (10 volts, 30 min) and 75 nm (20 volts, 30 min). This may suggest that higher voltages produce nano-hole membranes with bigger holes.

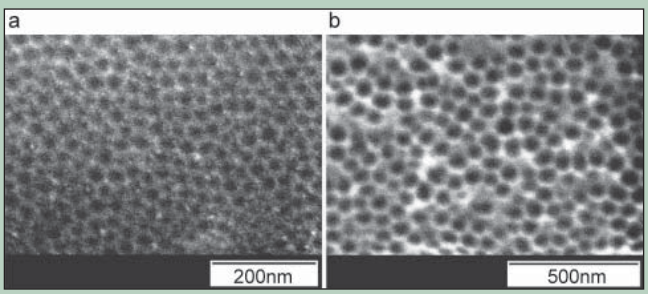

Figure 4. SEM images of semi-ordered nano-hole porous arrays. The pores range from 40 to 75 nm. (a) 10 volts, 30 min. (b) 20 volts, 30 min.

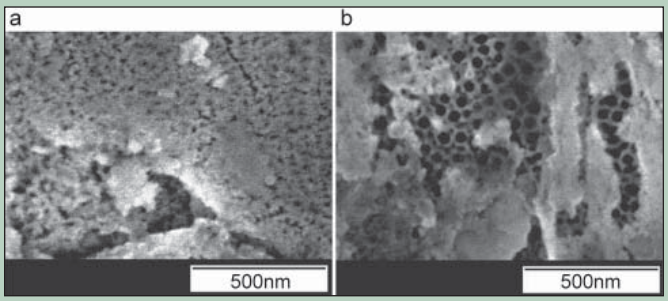

Figure 5. SEM images of (a) sponge-like ZrO_2 film and (b) mixed morphology. Note in (b) that underneath the sponge-like strips there are tubular nanostructures.

Samples with mixed morphologies (Figure 5) have been correlated to those that have been anodized for only a relatively short time. In this example, the samples were anodized for only 10 minutes, which was probably not enough time for the structure to fully and uniformly develop. From a mechanistic standpoint, those non-porous strips of oxide are remnants of the barrier oxide layer that is first formed when anodization is activated before it becomes a nanoporous or nanotubular structure. Since it usually takes very long anodization times to create a uniform nanoporous array, it makes sense that a sample anodized for 10 minutes shows remnants of the barrier oxide layer that has yet to begin seeding the growth of nanotubes.

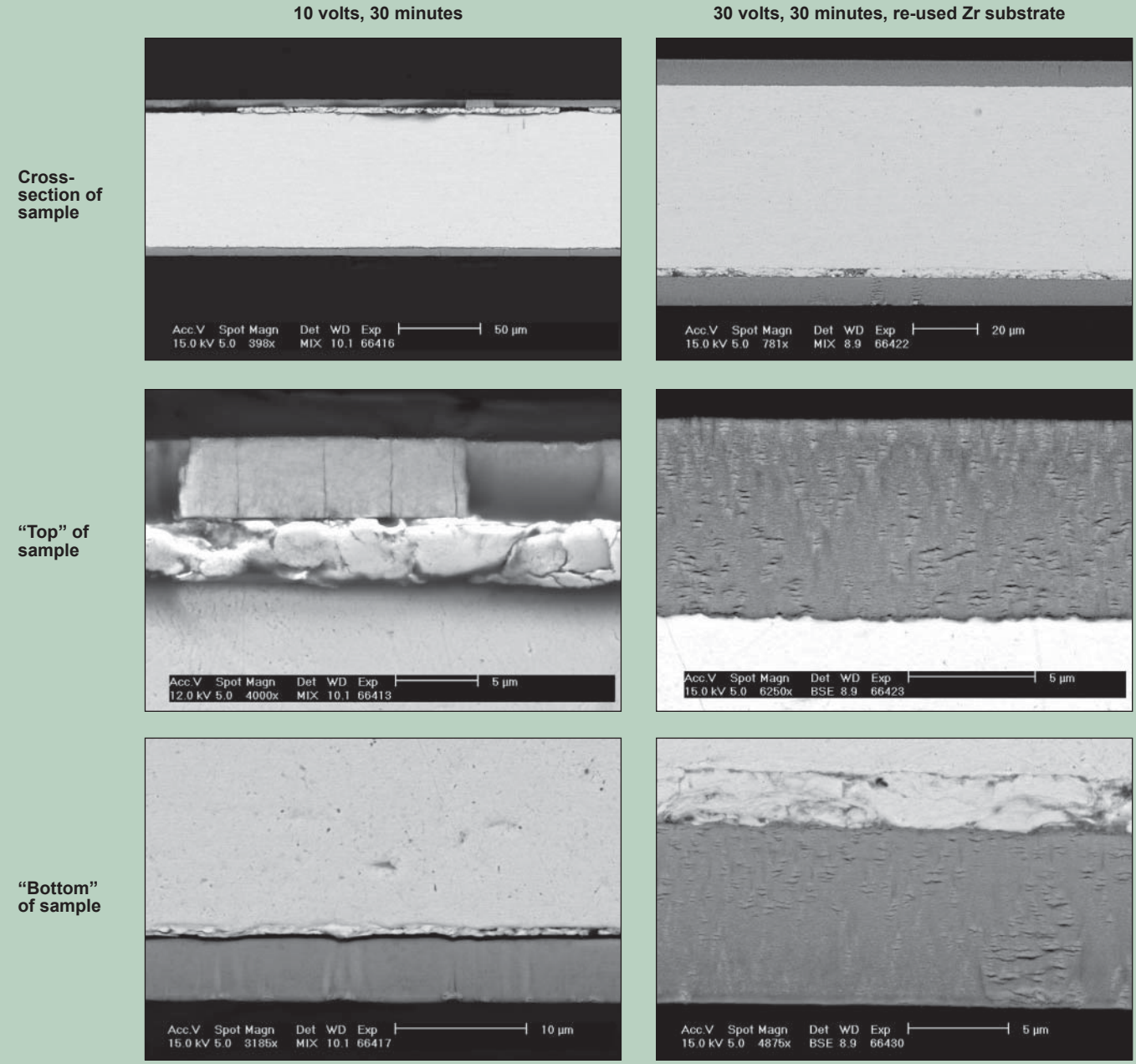

Figure 6. TEM images of the cross section of the samples made under 10 volts for 30 minutes (left column), and 30 volts for 30 minutes with a re-used Zr substrate (right column).

Finally, when analyzing the cross sections of the samples (Figure 6), ZrO_2 film can be observed on both sides of the zirconium substrate, which is logical because both sides of the zirconium are exposed in the electrolyte bath. The ZrO_2 film on the "top" layer of the 10 volts sample has cracks. The 30 volts sample on the left hand column exhibit interesting striations on the "top" and "bottom" ZrO_2 that indicate that the pores of the film are more penetrating. The thickness of the leftover substrate, which is the pale middle layer in the top row of pictures, is considerable in relation to thickness of the ZrO_2 film. On the other hand, it should be noted that the sample with the higher voltage has thicker ZrO_2 films. Both samples were anodized for half an hour, but the sample that was only anodized for 10 minutes created 4.4 μm thick ZrO_2 film, whereas the 30 minute sample produced ZrO_2 film that was approximately 9.6 μm thick. This is a logical relationship since higher applied voltages stimulate stronger and faster anodization, which is simply a type of electrochemical method.

Conclusion

Further research is needed to define and correlate the various ZrO_2 nanostructure morphologies to the specific processing variables. This way, one may be able to obtain the desired nanostructure morphology by simply tuning the parameters of the electrochemistry to the correct values. More studies should also be done on investigating the morphological results of different deposition regimes via permutations of voltage, duration, different electrolytes that can anodize zirconium. Meanwhile, additional steps that can refine the structure of the resulting ZrO_2 film like argon pre-anodization annealing to remove deformities should be capitalized in the future. The vertical profiles of the ZrO_2 film also deserve a closer look because the cracks and striations that are found give more information to the usefulness of ZrO_2 film applications. All of this may also be furthered with similar studies using "doped" Zr and compared with the pure Zr. Finally, investigation of other important characteristics such as ionic conductivity of the ZrO_2 is essential, especially because solid oxide fuel cells using ZrO_2 would operate by having oxygen ions flowing through it in order to convert chemical energy to electricity and heat.

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